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An Electrical Quadrupole Moment of the Deuteron

The Radiofrequency Spectra of HD and D_2 Molecules in a Magnetic Field*

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The molecular-beam magnetic-resonance method has been applied to study the radiofrequency spectra of the molecules D_2 and HD, in the state $J=1$. All the measurements were made in applied magnetic fields large enough to decouple the angular momentum vectors concerned. The spectrum of D_2 for the transitions $m_I=\pm 1$ consists of six lines as in H_2. The HD spectrum consists of two sets, one of nine lines in the region of the Larmor frequency of the proton, and another of twelve lines in the region of the Larmor frequency of the deuteron. The analyses of these spectra into sets of energy levels and a consistent theory are presented. As a consequence of the analysis one has to assume the existence in the deuteron of an electrical quadrupole moment, Q. The other quantities which are evaluated from these measurements are the spin-orbit interaction constants for the molecules concerned and the magnetic moments of the proton and deuteron, through the magnetic dipole-dipole interactions. The values of the constants are $Q=2.73\times 10^{-27}$ cm², $H'(D_2)=14.0$ gauss, $H'_D(\mathrm{HD})=20.1$ gauss, and $H'_P(\mathrm{HD})=20.48$ gauss. These spin-orbit interaction constants represent the magnetic field produced by the molecular rotation at the position of a nucleus. The values of the magnetic moments of the proton and deuteron agree with the direct measurements previously reported.

IN a previous note[1] we described experiments which indicated the existence of an electrical quadrupole moment of the deuteron. In this paper we shall present a more complete report of these and further experiments and of their interpretation.

It is hardly necessary to emphasize the particular importance for nuclear physics of the presence of an electrical quadrupole moment in the deuteron. Indeed, when these experiments were started there was no question of investigating such a quadrupole moment, because current theory predicted, under the assumption of central forces between the proton and neutron, that the deuteron is in a $^3S_1$ state which possesses no electrical dipole, quadrupole nor higher moment. The implication of the quadrupole moment is that the forces between proton and neutron in the deuteron are not "central."

Since the publication of the first note on the deuteron quadrupole moment the question has received theoretical discussion by a number of writers[2] who have examined the problem chiefly from the point of view of the meson theory of nuclear forces.

The possibility that a nuclear charge may depart from spherical symmetry was suggested by Racah[3] and by Pauli.[4] Schuler and Schmidt[5] were the first to present clear experimental evidence for such an effect, which they found in the departure from the interval rule of some lines in the hyperfine structure spectrum of europium.

The way in which a nuclear quadrupole moment manifests itself is through the fact that its energy in an external electric field depends not only on its position but also on its orientation with respect to the gradient of the field. In an atom the electric field is that of the electronic

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[1] J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, Jr. and J. R. Zacharias, Phys. Rev. **55**, 318 (1939).

[2] H. Bethe, Phys. Rev. **55**, 1261 (1939). R. F. Christy and S. Kusaka, Phys. Rev. **55**, 665L (1939). D. Inglis, Phys. Rev. **55**, 988L (1939); Phys. Rev. **55**, 329 (1939); Phys. Rev. **56**, 1175 (1939). E. Wigner and L. Eisenbud, Phys. Rev. **56**, 214 (1939). S. M. Dancoff, Phys. Rev. **56**, 385L (1939). P. Critchfield, Phys. Rev. **56**, 540 (1939). M. E. Rose, Phys. Rev. **56**, 1064 (1939). C. Kittel and G. Breit, Phys. Rev. **56**, 744 (1939). M. Phillips, Phys. Rev. **57**, 160 (1940).

[3] G. Racah, Zeits. f. Physik **71**, 431 (1931).

[4] W. Pauli, Zurich Conference, 1931.

[5] H. Schuler and Th. Schmidt, Zeits. f. Physik **94**, 457 (1935).

charge distribution. In a molecule the field arises from the other nuclei as well as from the electrons.

The quantum theory of the effect of a nuclear quadrupole moment on atomic energy levels was given by Casimir.[6] A similar theory for molecules can be constructed along analogous lines. The part of the energy operator which concerns the quadrupole moment of a nucleus is, according to Casimir,

$$e^2qQ\{3(\mathbf{i}\cdot\mathbf{J})^2+\tfrac{3}{2}(\mathbf{i}\cdot\mathbf{J})-i(i+1)J(J+1)\}/2J(2J-1)i(2i-1). \quad (1)$$

Q is the magnitude of the nuclear quadrupole moment and is given by $Q=\langle 3z^2-r^2\rangle_{\mathrm{Av}}$ and the average is taken over the nuclear charges for the state which has the largest component of the spin i in the z direction. The origin is at the centroid of the nucleus. The quantity $q=\langle \Sigma_k(3\cos^2\theta_k-1)/R_k{}^3\rangle_{\mathrm{Av}}$. The sum is taken over all of the molecular charges except the nucleus under discussion. The electrons contribute negatively. This average is taken over the state of the molecule which has the greatest component of its angular momentum J along the z direction. R_k is the distance of the kth element of charge from the nucleus in question. $\mathbf{J}$ and $\mathbf{i}$ are the molecular and nuclear angular momentum operators. θ_k is the angle which R_k makes with the z axis. The factor (qe) is the average of $\partial^2V/\partial z^2$ where V is the electrostatic potential at the nucleus.

The evaluation of our experimental results will give us the value of the product qQ. Unlike the atomic case there is no empirical information like fine-structure splitting from which the molecular q can be evaluated. One must[7] fall back on theoretical calculations from molecular wave functions to obtain q. Hence the value of Q must result partly from a calculation of q.

Since the effect of artificial external electric fields on a nuclear quadrupole moment is not measurable at present because of its very small size, it is impossible to measure quadrupole electric moments as directly as nuclear magnetic moments. The existence of a nuclear quadrupole moment is therefore at present an inference from the manner in which certain energy levels are shifted with respect to one another. In our experiments these shifts are of the same nature, in their manifestation, as those due to the magnetic dipole-dipole interaction between the two nuclei, and must therefore be disentangled from this type of interaction. However, this is not difficult, as we know the magnitudes of the magnetic moment of the proton and the deuteron and the internuclear distance.

A quadrupole moment effect is relatively large in our experiments whereas in atomic hyperfine structure studies the effect is generally small. For atomic deuterium in the ground state the effect vanishes because it is an S state for which q is zero. In excited states the effect would be smaller than the natural width of the energy level due to radiation damping. In general, in the atomic case, the quadrupole effect is superposed on the large interaction between the nuclear magnetic moment and the magnetic field produced by the electrons. These fields may be of the order of 10^6 gauss. In the D_2 and HD molecules which are the subject of our study these fields are well under 50 gauss. Since our resolving power[8] is about 10^5 times as great as with optical methods we can measure the effects of even the small magnetic fields in the molecule. The quadrupole effect is therefore relatively great because the gradient, "q," of the electric field which interacts with the quadrupole moment is of the same order of magnitude in molecules as in atoms.

METHOD

These investigations were carried out by the molecular beam magnetic resonance method.[9] The main features of this method as applied to gases were described in a previous paper[10] to which we will refer as I.

All of the spectra in paper I were observed in the following way: The radiofrequency oscillator was set at a definite constant frequency f_0 and the molecular beam intensity was observed as a

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[6] H. B. G. Casimir, "On the interaction between atomic nuclei and electrons," Prize Essay published by Teyler's Tweede Genootschap (1936).

[7] However, see E. Teller, Phys. Rev. **57**, 556(A) (1940).

[8] By resolving power we mean the smallest absolute interval in wave numbers in which two lines can be resolved, that is we mean $\Delta\nu$ rather than $\Delta\nu/\nu$.

[9] I. I. Rabi, S. Millman, P. Kusch and J. R. Zacharias, Phys. Rev. **55**, 529 (1939).

[10] J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, Jr. and J. R. Zacharias, Phys. Rev. **56**, 728 (1939).

function of the value of the homogeneous magnetic field H in which nonadiabatic transitions take place. At appropriate values of the magnetic field the beam intensity reaches a minimum and the various values of the magnetic field for which this occurs are called positions of the minima or positions of the lines. These minima occur whenever the product (hf_0) for the oscillator is equal to the difference in energy between two molecular states. The whole pattern of minima is referred to as the radiofrequency spectrum. In paper I we were chiefly concerned with the magnetic moments of the proton and of the deuteron. The measurements were made on HD and D_2 molecules in the state with rotational angular momentum $J=0$, and H_2 molecules in the state $J=1$. In the state $J=0$ the HD and the D_2 molecules each give rise to a one-line radiofrequency spectrum, for each nucleus. In the state $J=1$ the H_2 molecules give a 6-line spectrum in the frequency region in the neighborhood of the Larmor frequency of the proton, and another six-line spectrum in the region of the Larmor frequency of the rotational moment of the molecule. Only the first of these spectra was considered in I.

RESUMÉ OF H_2 RESULTS

In this paper we shall report on the nuclear radiofrequency spectra of HD and D_2 molecules in the state $J=1$, and on our analysis of these spectra. Since the treatment of D_2 as given here is so much like that of H_2 as given in I, and since we wish to make use of certain of the H_2 results in the discussion of the analysis of the D_2 spectrum, we give here a brief resumé of the important features and results of the H_2 analysis.

The H_2 experiments were performed on a beam of molecules emerging from a liquid-nitrogen-cooled source. Parahydrogen molecules at liquid-nitrogen temperatures are practically all in the state $J=0$ and have the total nuclear spin $I=0$. They are inert as far as our experiments are concerned, so that our study of H_2 was made on orthohydrogen molecules in the state $J=1$, $I=1$. In this state there are $(2J+1)(2I+1)=9$ energy levels. Because of the selection rule $\Delta m_I=\pm 1$ for transitions with $\Delta m_J=0$, there are 6 transitions allowed between these levels giving rise to the six-line nuclear spectrum. We were able to analyze this six-line radiofrequency spectrum and thereby obtain values for two important physical quantities: 1, the value of $\langle \mu_P/r^3\rangle_{\text{Av}}$ (called H'') which appears because of the dipole-dipole magnetic interaction between the two protons; and 2, the magnetic field H' produced by the molecular rotation at the position of a nucleus. More properly H' is the constant in the expression for the spin-orbit interaction of the proton moments with the molecular rotation. In high magnetic fields with correspondingly high oscillator frequency, the six lines for H_2 are symmetrically disposed with respect to H_0 (defined by $H_0\equiv hf_0/2\mu_P$) and with no minimum at the position H_0. Assuming complete Paschen-Back effect, the positions of the minima are given by the following simple formulae:

$$H_0\pm(3S_P+H'); \quad H_0\pm(3S_P-H'); \quad H_0\pm 6S_P,$$

where S_P is related to H'' by $S_P=\frac{1}{5}H''$. The values obtained for these quantities were $H'=27.2$ gauss and $S_P=6.8$ gauss.

These *two* constants, H' and S_P, are sufficient to account for the positions of all *six* lines and for the variations in their position with gross changes of field. Furthermore the constant H'' can be calculated from the known value of the proton moment and the known internuclear distance of H_2. This value agrees with the experimental value of H''. The consistency and reasonableness of the analysis of the H_2 spectrum shows that we have not omitted any important features of the molecular constitution in setting down the fundamental equation on which our analysis rests.

THE D_2 SPECTRUM

Turning now to the discussion of the D_2 molecule we take note of the following facts. The D_2 molecule is homonuclear, the nuclei have spins of one and obey the Bose statistics. The lowest rotational state of D_2 is therefore a state in which the wave function of the nuclear spins is symmetrical and the total spin angular momentum I, is either zero or two. For the next higher rotational state, $J=1$, (para-D_2) the wave function for the two nuclear spins must be antisymmetrical and the total spin angular momentum is 1. For the state $J=2$ the wave function is again symmetrical and I is either zero or two. At liquid-nitrogen temperatures almost all the molecules are in these states and they are therefore the only ones we need consider. (See Table I of paper I).

This may most easily be done under the classification of their total rotational angular momentum and spin:

1. $J=0$, $I=0$. 9.3 percent of the beam. These molecules are inert in our apparatus since they have no magnetic moment.

2. $J=0$, $I=2$. 46.7 percent of the beam. These molecules give rise to the deep central minimum which is so prominent on any of the D_2 nuclear curves and which was used in paper *I* for the determination of the deuteron magnetic moment.

3. $J=2$, $I=2$. 8.7 percent of the beam. These molecules are divided among $(2J+1)(2I+1)=25$ energy states in a strong magnetic field. Thus each state contains 0.35 percent of the molecules. The selection rule $\Delta m_I=\pm 1$, for $\Delta m_J=0$ gives, for each m_J level, 4 possible transitions. Thus there should be a total of 20 transitions possible. Since in our experiments transitions from level b to level a are counted as well as those from a to b, there would be 0.7 percent of the total beam in each of these 20 minima. However the effect of the velocity distribution operates to decrease this intensity by about 25 percent, and since, using a D_2 beam our apparatus will not detect changes of beam intensity of less than $\frac{1}{2}$ percent of the total beam, we did not expect to observe, and did not observe any minima from molecules in this state.

4. $J=2$, $I=0$. 1.7 percent of the beam. The same considerations apply here as far as intensity is concerned as to the molecules in state $J=2$, $I=2$. Furthermore the only transitions possible are those for which $\Delta m_J=\pm 1$ and this would give rise to lines in the rotational spectrum.

5. $J=1$, $I=1$. 33 percent of the beam. These are the molecules with which we are concerned in the experiments on D_2 reported in this paper. In a strong magnetic field there are $2J+1=3$ possible orientations of J and for each of these $2I+1=3$ possible orientations of I; altogether 9 states. Each energy state should therefore contain 3.7 percent of the molecules of the beam. Between these 9 levels there should be 6 possible transitions corresponding to changes of m_I of ± 1 while m_J remains unchanged. If the effect of the velocity distribution is neglected the intensity of each of these minima should therefore be 7.4 percent of the total beam intensity. If the effect of the velocity distribution is included this intensity should drop to about 5.4 percent of the total beam intensity.

Thus, excepting the intensity considerations, the situation for para-D_2 molecules in the state $J=1$, $I=1$ is exactly that which obtained for ortho-H_2 molecules as discussed in paper I. Because of our knowledge of the H_2 constants, we expected to be able to predict the positions of the six D_2 minima at least approximately. This should be made clearer by the following discussion.

PRELIMINARY DISCUSSION OF D_2 SPECTRUM

In the section called theory we will derive expressions for the nine energy levels (given in Table I) of para-D_2 on the assumption that there are three types of interaction to consider, i.e., spin-orbit, with constant H'; spin-spin, with constant H''; and nuclear electric quadrupole, with constant H'''. The possible transitions between these energy levels are given in Table II. Inspection of this table shows that if the electric quadrupole interaction constant, H''', is set equal to zero, the transitions between the energy levels for D_2 will be represented by exactly the same expressions as for H_2. The values of the constants

TABLE I. *Energy levels correct to the third-order perturbations for the first rotational state of para-*D_2 *molecules in a magnetic field. The terms in* H' *and* S_D *give the first-order perturbation, the terms in* C_2 *and* C_2' *the second, and the terms in* C_3 *the third. The definitions of the quantities are as follows:*

$$S_D=\tfrac{1}{5}(H''+H''');\quad \alpha=\mu_R/\mu_D=0.440/0.855=0.515;$$
$$C_2=[(H'+3S_D)^2+18S_D^2]/(1-\alpha)H;$$
$$C_2'=(H'-3S_D)^2/(1-\alpha)H;$$
$$C_3=(H'+3S_D)^2(H'-9S_D)/(1-\alpha)^2H^2;$$
$$H''=\langle\mu_D/r^3\rangle_{\text{Av}};\quad H'''=(-5e^2qQ/4\mu_D).$$

m_J	m_I	ENERGY
1	1	$-\mu_D(H+\alpha H+H'-S_D)$
1	0	$-\mu_D(+\alpha H+2S_D-C_2')$
1	−1	$-\mu_D(-H+\alpha H-H'-S_D-C_2+C_3)$
0	1	$-\mu_D(H+2S_D+C_2')$
0	0	$-\mu_D(-4S_D-2C_3)$
0	−1	$-\mu_D(-H+2S_D-C_2')$
−1	1	$-\mu_D(H-\alpha H-H'-S_D+C_2+C_3)$
−1	0	$-\mu_D(-\alpha H+2S_D+C_2')$
−1	−1	$-\mu_D(-H-\alpha H+H'-S_D)$

H' and S_D will of course be different, but these should be readily calculable from the known values of the constants for H_2. The spin-orbit constant, H', can be taken to be one-half of that for hydrogen since the angular velocity of rotation of the D_2 molecule is half as great and the internuclear distances are so nearly the same for the two molecules. We can make this assumption with some confidence because it has been shown experimentally[11] that the ratio of the rotational magnetic moments of the two molecules is 2 to 1. Similarly the value of the spin-spin constant $H''=\langle\mu_D/r^3\rangle_{Av}$ can be obtained for D_2 since (μ_D/μ_P) and μ_P/r^3 are both known. These constants then become $H'=13.6$ gauss and $H''=10.5$ gauss. $S_D=H''/5=2.1$ gauss. Inserting these values into the expressions given above for H_2 we obtain the predicted spectrum with minima as indicated by vertical lines in Fig. 1.

The complete lack of correspondence between the experimental and predicted curves is somewhat startling, especially so when one recalls how well the theory fits the case of H_2. As is evident from the figure it was expected that the six-line D_2 spectrum would fall within the wings of the deep central minimum arising from the state $J=0$, since the ratio of the depths of the small to the large minima is 1 to 7.

It was suspected that the discrepancy between theory and experiment was due to a quadrupole moment of the deuteron.

The apparatus was remodeled to increase the resolving power for a more accurate study of the phenomenon. It was shown in paper I that the resolving power of our apparatus depends upon the length of time that the molecule remains under the influence of the radiofrequency field. In fact, the minimal half-width (width, ΔH, in gauss at half-depth) for a transition without any fine structure is given by $\Delta H=hIv/\mu L$ where L is the length of the radiofrequency field and v is the velocity of the molecule traversing the field. At the time the experimental curve of Fig. 1 was taken the path of the molecules in this field was 2.7 cm. We calculate for this length of field and for D_2 at 80°K the minimal half-width of a line as predicted by the above equation to be about 30 gauss. By increasing the length of the radiofrequency field to 13.5 cm this minimal half-width can be cut down by a factor of 5.

TABLE II. *Changes of energy associated with the change of orientation of the total nuclear spin by ±1 for para-*D_2 *molecules in the first rotational state.* $S_D=\frac{1}{5}(H''+H''')$.

m_J	m_I	$\Delta E/\mu_D$
1	$0\rightarrow1$	$H+H'-3S_D+0\ +C_2'+0$
1	$-1\rightarrow0$	$H+H'+3S_D+C_2-C_2'-\ C_3$
0	$0\rightarrow1$	$H+0\ +6S_D+0\ +C_2'+2C_3$
0	$-1\rightarrow0$	$H+0\ -6S_D+0\ +C_2'-2C_3$
−1	$0\rightarrow1$	$H-H'-3S_D+C_2-C_2'+\ C_3$
−1	$-1\rightarrow0$	$H-H'+3S_D+0\ +C_2'+0$

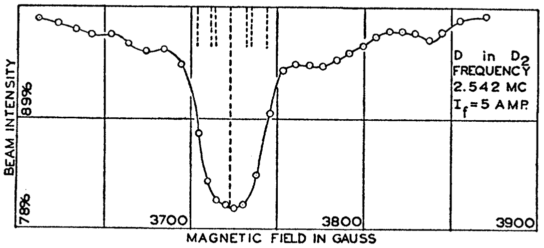

FIG. 1. Radiofrequency spectrum of D_2 at 80°K for changes of total spin magnetic quantum number m_I of ±1 with m_J unchanged. This curve was taken at a time when the length of the radiofrequency field was only 2.7 cm. The spectrum predicted on the assumption of no quadrupole moment is indicated by the dotted lines, both as to position and relative intensity. The theoretical minimal half-width for any of these minima, 30 gauss, is in good agreement with the observed curve.

The apparatus was accordingly lengthened. The deflecting magnets were separated enough to allow for a homogeneous field 15 cm long. This magnet and its radiofrequency field wires were also used in the experiments of paper I.

The curve of Fig. 2 represents data obtained with the improved conditions. The subsidiary minima are resolved from each other and from the central minimum. The positions of the secondary minima are in violent disagreement with the provisional theory outlined above. In fact the interval between the extreme lines is six times greater than was expected.

DETAILED DISCUSSION OF D_2 SPECTRUM

A set of energy levels which accounts completely for these lines will be developed in the section called "Theory of energy levels" of D_2. The only assumption in addition to those made for H_2 is that a nuclear electric quadrupole interacts with the molecular electric field. The nine energy levels for D_2 in the first rotational state

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[11] N. F. Ramsey, Jr., Phys. Rev. **55**, 595 (1939).

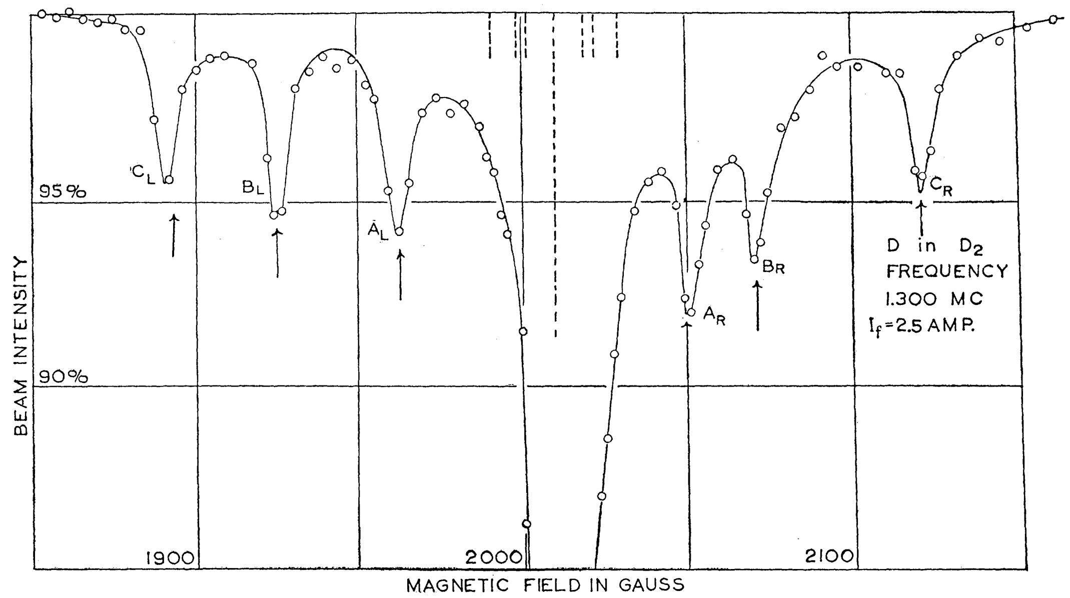

FIG. 2. Radiofrequency spectrum of D_2 at 80°K for $\Delta m_I=\pm 1$, with m_J unchanged. The length of the radiofrequency field is 13.5 cm. Dotted lines indicate spectrum predicted on the assumption of no quadrupole moment. Arrows indicate positions of lines predicted from the complete theory and the constants from the 2.419-MC data. Theoretical minimal half-width for any of these minima is about 6 gauss. The central minimum is not symmetrical about the central dotted line because of the method of producing the radiofrequency field, as discussed by S. Millman (Phys. Rev. **55**, 628 (1939)). If the directions of all of the static magnetic fields are reversed, the asymmetry is reversed. This result was used to show that the deuteron magnetic moment is positive.

are given in Table I which is complete up through the third order of the perturbation theory expanded about the strong field levels. The terms in H' and S_D to the first power are the first-order perturbations produced by the three types of interaction mentioned above. These terms are independent of field and remain even in the presence of a large applied field. The terms C_2 and C_2' are second-order terms which are inversely proportional to H and therefore vanish in high fields. They arise because of incomplete Paschen-Back effect or incomplete decoupling of the total nuclear spin and the molecular rotation. The same is true of the third-order terms C_3 except that the decrease with increasing field is even more rapid. Throughout the following discussion the terms in C_3 can and will be neglected.

Energy differences for transitions of m_I of ± 1 with m_J held constant are listed in Table II. Dividing the terms of Table II through by μ_D and setting $\mu_D H_0 = hf_0$ we obtain expressions for the positions of the lines for the frequency f_0 as given in Table III.

As in paper I we can use the asymmetry of the positions of the minima to identify the individual lines with the quantum numbers of the transitions given in Table III. This identification can be made unambiguously from the 2.419-MC data of Table IV, since, for the fields at which these transitions occur, all perturbations higher than second order have no appreciable effect, and the only terms which render the pattern unsymmetrical are C_2 and C_2'. It can be seen from Table III that four of the lines should be shifted from symmetrical positions about H_0 by amounts $-C_2'$ while two other lines are shifted by amounts $-(C_2-C_2')$. Thus the midpoint between one pair of lines should be shifted from the position H_0 by $-(C_2-C_2')$ while the midpoints of two other pairs should be shifted from H_0 by amounts $-C_2'$.

This is just the type of shift which is found experimentally as can most easily be seen from the 2.419-MC data as follows:

$$\tfrac{1}{2}(C_R+C_L)-H_0=-0.9 \text{ gauss},$$
$$\tfrac{1}{2}(B_R+B_L)-H_0=-6.0 \text{ gauss},$$
$$\tfrac{1}{2}(A_R+A_L)-H_0=-1.1 \text{ gauss}.$$

We see from this that the B minima correspond to the second and fifth rows of Table IV, and therefore that $(C_2'-C_2)$ is about 6 gauss. Similarly since the A and C minima correspond to the other rows we conclude that C_2' is approximately 1 gauss. Substituting this value and $H=3700$ gauss into the expression for C_2' we can arrive at a preliminary rough value for $(3S_D-H')$ of ± 43 gauss. Since the A minima are displaced from H_0 by very nearly that amount and the C minima by much more we can take the interval between the A minima of 90.3 gauss as $2(3S_D-H')$. Thus the A minima correspond to the third and fourth rows of Table III. This leaves the C minima to go with the first and sixth rows. We can now summarize as follows:

$$2(3S_D-H')=A_R-A_L=90.3 \text{ gauss},$$
$$2(3S_D+H')=B_R-B_L=147.0 \text{ gauss},$$
$$2(6S_D)=C_R-C_L=234.2 \text{ gauss}.$$

In the above summary we have taken S_D and H' as positive for the following reason. Since $(3S_D-H')$ is numerically less than $(3S_D+H')$ we conclude that S_D and H' must have the same sign. Now we know that H' is positive because it is the spin orbit constant for D_2 and would have the same sign as the corresponding spin-orbit constant for H_2, which was shown in paper I to be positive. From this consideration we will later derive the sign of qQ. This completes the identification and the detailed assignment of quantum numbers as given in Table III.

In order to evaluate the constants H' and $3S_D$ from the data as precisely as possible the following procedure was adopted. First a preliminary evaluation was made from the equations above. These values were used to evaluate the constants C_2, C_2' and C_3 as given in Table V. With these constants and the 2.419-MC data of Table IV a set of six equations linear in H' and $3S_D$ can be set up and solved by the method of least squares. The values obtained this way are

$$H'=14.00 \text{ gauss} \quad \text{and} \quad 3S_D=58.86 \text{ gauss}.$$

TABLE III. *Magnetic fields for which resonances will occur for changes of orientation of the total nuclear spin by ±1 for para-*D_2 *molecules in the first rotational state.* $H_0=hf_0/\mu_D$.

m_J	m_I	MAGNETIC FIELD IN GAUSS	LINE DESIGNATION
1	$0\leftrightarrow 1$	$H_0-H'+3S_D-C_2'+0\ +0$	A_R
1	$-1\leftrightarrow 0$	$H_0-H'-3S_D+C_2'-C_2+\ C_3$	B_L
0	$0\leftrightarrow 1$	$H_0+0\ -6S_D-C_2'+0\ -2C_3$	C_L
0	$-1\leftrightarrow 0$	$H_0+0\ +6S_D-C_2'+0\ +2C_3$	C_R
−1	$0\leftrightarrow 1$	$H_0+H'+3S_D+C_2'-C_2-\ C_3$	B_R
−1	$-1\leftrightarrow 0$	$H_0+H'-3S_D-C_2'-0\ +0$	A_L

The general consistency of the experiment with the theory is best exhibited in Table V. The two experimental parameters H' and $3S_D$ are used to predict the positions of the six minima. The greatest deviation between the calculated and experimental values is 0.5 gauss. This is better than 1 gauss, the estimated probable error in the determination of a minimum. The second-order perturbations as evaluated experimentally above are 1 gauss for the A and C minima and 6 gauss for the B minima. These are to be compared with the theoretical values of 1.1 gauss, and 5.6 and 5.9 gauss given in Table V.

Further agreement of experiment with the theory is provided by the 1.300-MC data as exhibited in Table VI. The constants H' and $3S_D$ as evaluated above from the 2.419-MC data have been used for predicting the positions of the lines for the frequency of 1.300 MC. Table VI shows that for these low fields (approximately 2000 gauss) the perturbation theory used does not converge. For the minima C_R and C_L the third order is as large as the second. It was therefore necessary to calculate the energy levels directly from the secular equation and to find the positions of the minima from them. For four of the lines the agreement between predicted position and experimental position is unusually good, whereas for the other two lines the agreement is just within the sums of the limits of error for the

TABLE IV. *Displacements in gauss for minima of para-*D_2 *from* H_0*, the central minimum of ortho-*D_2*. These displacements are considered reliable to ±1 gauss for the 2.419-MC data and to ±1.5 gauss for the 1.300-MC data. Note that* B_L *and* B_R *are much more unsymmetrically placed than the others; that they are all more symmetrical in the higher field,* $H_0=3710$ *gauss.*

DESIGNATION OF MINIMUM	DISPLACEMENTS IN GAUSS FOR OSCILLATOR FREQUENCIES OF 2.419 MC	1.300 MC
C_L	−118.0	−118.0
B_L	− 79.5	− 84.0
A_L	− 46.3	− 47.6
H_0	(3710)	(1995)
A_R	44.0	40.7
B_R	67.5	61.3
C_R	116.2	112.0

TABLE V. *This table shows the magnitudes of the calculated perturbations of the lines in the D in* D_2 *spectrum at 2.419 MC and the comparison with the experimentally found perturbations. The "Line Designations" are those assigned to the minima of Fig. 2.*

PERTURBATIONS				LINE DESIGNATION AND EXPERIMENTAL PERTURBATION
FIRST ORDER	SECOND ORDER	THIRD ORDER	TOTAL	
$6S_D$ 117.7	$-4140/H$ -1.1	$-7.3\times 10^6/H^2$ -0.4	116.2	C_R 116.2
$3S_D+H'$ 72.9	$-21{,}300/H$ -5.6	$3.6\times 10^6/H^2$ 0.2	67.5	B_R 67.5
$3S_D-H'$ 44.9	$-4140/H$ -1.1	0 0	43.8	A_R 44.0
$-(3S_D-H')$ -44.9	$-4140/H$ -1.1	0 0	-46.0	A_L -46.3
$-(3S_D+H')$ -72.9	$-21{,}300/H$ -5.9	$-3.6\times 10^6/H^2$ -0.2	-79.0	B_L -79.5
$-6S_D$ -117.7	$-4140/H$ -1.2	$7.3\times 10^6/H^2$ 0.4	-118.5	C_L -118.0

constants and the experimental determination of the minima. This is most likely due to the fact that the 1.300-MC data were taken only once, whereas the 2.419-MC data are the result of averaging several runs.

The quantity S_D is defined as $\frac{1}{5}(H''+H''')$ so that the experiment with D_2 is incapable of providing a determination of either H'' or H''' separately. We can, however, take the value of H'' from the experiment on H_2 as discussed above. That value of H'' of 10.5 gauss subtracted from $5S_D=98.1$ gauss yields 87.6 gauss for H'''. It is to be noted that this value of H''' is positive. The significance of this quantity will be discussed later.

EXPERIMENTS ON HD

Experiments on HD were undertaken to prove that the quantity H''' is certainly a property of the deuterium nucleus and is not just a peculiarity of the D_2 molecule. This proof takes the following simple form. In HD one set of transitions can occur for changes of the magnetic quantum number for the proton and another set for the deuteron. In the first case the pattern should be completely accounted for without any necessity for considering a quadrupole moment of the deuteron because even if such a quantity does exist the changes of energy of the molecule accompanying changes of m_P would not be affected thereby. This follows, since if no reorientation of the deuteron occurs within the molecule relative to the extranuclear electrical configuration, no changes of energy would occur. On the other hand, if we consider the transitions of m_D, then such energy changes should occur, and the spectrum should show the presence of the quadrupole moment. As this turns out to be the case these experiments show that the effect is a property of the deuteron and not some molecular property.

Furthermore in HD the spin-spin and quadrupole interactions can be evaluated experimentally and therefore *the value of the deuteron quadrupole moment will not depend on subtracting a calculated quantity,* H'', *as in* D_2. A further check on the correctness of the theory will be afforded by a comparison of the interaction constants obtained with HD with those previously obtained with H_2 and D_2.

NUCLEAR SPECTRA OF HD

The HD molecule is heteronuclear and there is no quantum number of total spin. There are therefore three coupled angular momenta J, I_D and I_P with projections for the strong field case of m_J, m_D, and m_P. At the temperature of liquid N_2, 63 percent of the molecules are in the state $J=0$, and for this state all interactions of the type discussed in this paper average out to zero. These molecules are therefore ideally suited to the determination of the nuclear magnetic moments of the proton and the deuteron but are of no use at all in the present experiment except for the location of $H_0=hf_0/\mu$. The remaining 37 percent of the molecules are in the state $J=1$, only 0.3 percent being in the state $J=2$. Therefore any fine structure that is observed is immediately attributable to the molecules in the

TABLE VI. *Comparison of experimental D in* D_2 *perturbations at 1.300 MC with the perturbations as calculated with the constants obtained from the 2.419-MC data of D in* D_2.

LINE DESIGNATION	PERTURBATIONS PREDICTED FROM 2.419-MC D_2 DATA				EXPERIMENTAL VALUE
	FIRST ORDER	SECOND ORDER	THIRD ORDER	SECULAR	
C_R	117.7	-1.96	-1.63	113.0	112.0
B_R	72.9	-10.36	.86	63.7	61.3
A_R	44.9	-2.04	0.00	43.0	40.7
A_L	-44.9	-2.12	0.00	-47.4	-47.6
B_L	-72.9	-11.11	-1.00	-84.6	-84.0
C_L	-117.7	-2.20	2.07	-117.7	-118.0

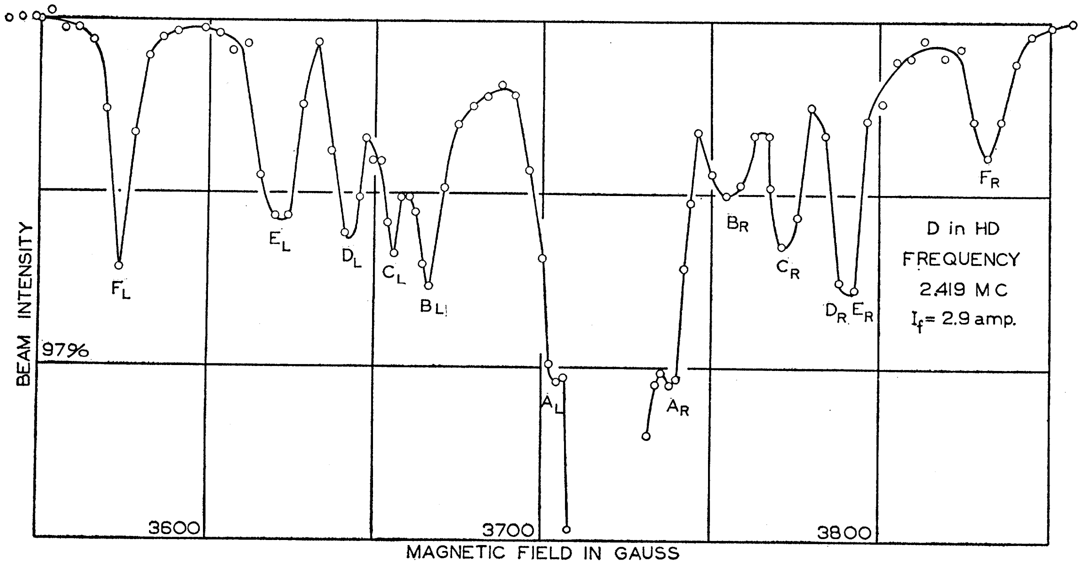

FIG. 3. Radiofrequency spectrum of HD at 80°K for $\Delta m_D = \pm 1$ with m_P and m_J unchanged.

state $J=1$. In a strong magnetic field there are three orientations of J, three orientations of the deuteron spin, and two orientations of the proton spin. This makes eighteen possible states which in strong field gives eighteen different energy levels. There are three types of transitions among these energy levels, i.e., (1) those for which m_D changes by ± 1 giving twelve different transitions; (2) those for which m_P changes by ± 1 giving rise to nine different transitions; and (3) those for which m_J changes by ± 1 giving twelve different transitions. The first group (called D in HD) clusters around $H_0 = hf_0/\mu_D$ and will be discussed first. The second group (called H in HD) clusters around $H_0 = hf_0/2\mu_P$ and will be discussed next. The third group which clusters around $H_0 = hf_0/\mu_R$ will be discussed in a separate paper devoted to the general question of rotational magnetic moments.

D IN HD

Figure 3 shows the group of minima associated with changes of m_D of ± 1 at the frequency of 2.419 MC. The deep central minimum is not completely shown in the graph so that the small minima for $J=1$ will show to better advantage. Besides the central minimum there are eleven clearly resolved minima one of which is taken to be double since twelve are expected altogether.

The experimental procedure for taking this curve is similar to that for the other data except that for this case particular attention has to be paid to the magnitude of the deflecting and refocusing fields. In the HD molecule the deflections are chiefly due to the large proton moment so that if a very large deflecting field is used to affect the motion of the molecule by action on the smaller deuteron moment the excursions produced by the proton moment are so large that the refocusing conditions are not good. Therefore a compromise is sought before the data is taken for one curve.

The column labeled "Experimental" in Table IX represents the average of two sets of data for D in HD at the one frequency.

In the section called "Theory of energy levels of HD" we will derive expressions for the eighteen energy levels of HD in the first rotational state on the assumption that there are three types of interaction to consider, i.e., spin-orbit interaction of the deuteron with the magnetic field of the molecular rotation at the position of the deuteron and the similar type for the proton, with interaction constants $\mu_D H'_D$ and $2\mu_P H'_P$; spin-spin interaction of the deuteron with the proton with interaction constant $S = \langle 2\mu_P\mu_D/5r^3\rangle_{\text{Av}}$; and the interaction of the deuteron quadrupole moment with the gradient of the electric field with inter-

TABLE VII. *Energy levels for* HD *molecules in the first rotational state. The energies are in gauss nuclear magnetons if* μ_R, μ_P, *and* μ_D *are given in nuclear magnetons. This notation is used because the second- and third-order expressions are given numerically using experimental values for the constants* H'_P, H'_D, S, *and* E. $S=\langle 2\mu_P\mu_D/5r^3\rangle_{\mathrm{Av}}$. $E=H'''/5=e^2Q/4\mu_D$.

			ENERGY IN GAUSS NUCLEAR MAGNETONS			
m_J	m_P	m_D	ZEROTH ORDER	FIRST	SECOND	THIRD
1	$\frac{1}{2}$	1	$-\mu_PH\ -\mu_DH\ -\mu_RH$	$-\mu_PH'_P\ -\mu_DH'_D + S - \mu_DE$	$+0$	$+0$
1	$\frac{1}{2}$	0	$-\mu_PH\ -\mu_RH$	$-\mu_PH'_P\ +2\mu_DE$	$+10{,}160/H$	$+1.75\times10^6/H^2$
1	$\frac{1}{2}$	-1	$-\mu_PH\ +\mu_DH\ -\mu_RH$	$-\mu_PH'_P\ +\mu_DH'_D - S - \mu_DE$	$+30{,}660/H$	$+6.35\times10^6/H^2$
1	$-\frac{1}{2}$	1	$+\mu_PH\ -\mu_DH\ -\mu_RH$	$+\mu_PH'_P\ -\mu_DH'_D - S - \mu_DE$	$+621/H$	$+0$
1	$-\frac{1}{2}$	0	$+\mu_PH\ -\mu_RH$	$+\mu_PH'_P\ +2\mu_DE$	$+34{,}400/H$	$-4.75\times10^6/H^2$
1	$-\frac{1}{2}$	-1	$+\mu_PH\ +\mu_DH\ -\mu_RH$	$+\mu_PH'_P\ +\mu_DH'_D + S - \mu_DE$	$+23{,}600/H$	$-8.24\times10^6/H^2$
0	$\frac{1}{2}$	1	$-\mu_PH\ -\mu_DH$	$-2S\ +2\mu_DE$	$-10{,}780/H$	$-1.75\times10^6/H^2$
0	$\frac{1}{2}$	0	$-\mu_PH$	$-4\mu_DE$	$-11{,}110/H$	$+2.14\times10^6/H^2$
0	$\frac{1}{2}$	-1	$-\mu_PH\ +\mu_DH$	$+2S\ +2\mu_DE$	$+30{,}400/H$	$+4.72\times10^6/H^2$
0	$-\frac{1}{2}$	1	$+\mu_PH\ -\mu_DH$	$+2S\ +2\mu_DE$	$-30{,}400/H$	$+4.72\times10^6/H^2$
0	$-\frac{1}{2}$	0	$+\mu_PH$	$-4\mu_DE$	$+11{,}110/H$	$+2.14\times10^6/H^2$
0	$-\frac{1}{2}$	-1	$+\mu_PH\ +\mu_DH$	$-2S\ +2\mu_DE$	$+10{,}780/H$	$-1.75\times10^6/H^2$
-1	$\frac{1}{2}$	1	$-\mu_PH\ -\mu_DH\ +\mu_RH$	$+\mu_PH'_P\ +\mu_DH'_D + S - \mu_DE$	$-23{,}600/H$	$-8.24\times10^6/H^2$
-1	$\frac{1}{2}$	0	$-\mu_PH\ +\mu_RH$	$+\mu_PH'_P\ +2\mu_DE$	$-34{,}400/H$	$-4.75\times10^6/H^2$
-1	$\frac{1}{2}$	-1	$-\mu_PH\ +\mu_DH\ +\mu_RH$	$+\mu_PH'_P\ -\mu_DH'_D - S - \mu_DE$	$-621/H$	$+0$
-1	$-\frac{1}{2}$	1	$+\mu_PH\ -\mu_DH\ +\mu_RH$	$-\mu_PH'_P\ +\mu_DH'_D - S - \mu_D\mu$	$-30{,}660/H$	$+6.34\times10^6/H^2$
-1	$-\frac{1}{2}$	0	$+\mu_PH\ +\mu_RH$	$-\mu_PH'_P\ +2\mu_DE$	$-10{,}160/H$	$+1.75\times10^6/H^2$
-1	$-\frac{1}{2}$	-1	$+\mu_PH\ +\mu_DH\ +\mu_RH$	$-\mu_PH'_P\ -\mu_DH'_D + S - \mu_DE$	$+0$	$+0$

TABLE VIII. *Magnetic fields at which resonances will occur for changes of orientation of the deuteron spin in* HD *molecules in the first rotational state.* $H_0=hf_0/\mu_D$. $S'=\langle 2\mu_P/5r^3\rangle_{\mathrm{Av}}$

			MAGNETIC FIELDS AT WHICH RESONANCES OCCUR			
m_J	m_P	Δm_D		FIRST ORDER	SECOND ORDER	THIRD ORDER
1	$\frac{1}{2}$	$0\Leftrightarrow1$	H_0	$-H'_D + S'-3E$	$-11{,}900/H$	$-2.05\times10^6/H^2$
1	$\frac{1}{2}$	$-1\Leftrightarrow0$	H_0	$-H'_D + S'+3E$	$-24{,}000/H$	$-5.38\times10^6/H^2$
1	$-\frac{1}{2}$	$0\Leftrightarrow1$	H_0	$-H'_D - S'-3E$	$-39{,}500/H$	$+5.56\times10^6/H^2$
1	$-\frac{1}{2}$	$-1\Leftrightarrow0$	H_0	$-H'_D - S'+3E$	$+12{,}600/H$	$+4.09\times10^6/H^2$
0	$\frac{1}{2}$	$0\Leftrightarrow1$	H_0	$-2S'+6E$	$+386/H$	$-4.55\times10^6/H^2$
0	$\frac{1}{2}$	$-1\Leftrightarrow0$	H_0	$-2S'-6E$	$-48{,}500/H$	$-3.02\times10^6/H^2$
0	$-\frac{1}{2}$	$0\Leftrightarrow1$	H_0	$+2S'+6E$	$-48{,}500/H$	$+3.02\times10^6/H^2$
0	$-\frac{1}{2}$	$-1\Leftrightarrow0$	H_0	$+2S'-6E$	$+386/H$	$+4.55\times10^6/H^2$
-1	$\frac{1}{2}$	$0\Leftrightarrow1$	H_0	$+H'_D + S'-3E$	$+12{,}600/H$	$-4.09\times10^6/H^2$
-1	$\frac{1}{2}$	$-1\Leftrightarrow0$	H_0	$+H'_D + S'+3E$	$-39{,}500/H$	$-5.56\times10^6/H^2$
-1	$-\frac{1}{2}$	$0\Leftrightarrow1$	H_0	$+H'_D - S'-3E$	$-24{,}000/H$	$+5.38\times10^6/H^2$
-1	$-\frac{1}{2}$	$-1\Leftrightarrow0$	H_0	$+H'_D - S'+3E$	$-11{,}900/H$	$+2.05\times10^6/H^2$

TABLE IX. *Collected data on D in* HD. *Frequency 2.419 MC.*

			PERTURBATIONS						
			PREDICTED FROM H_2 AND D_2 CONSTANTS						
m_J	m_P	m_D	FIRST ORDER	SECOND ORDER	THIRD ORDER	TOTAL	EXPERIMENTAL VALUE	LINE DESIGNATION	PERTURBATIONS FROM HD CONSTANTS
1	$\frac{1}{2}$	$0\Leftrightarrow1$	-59.11	-3.26	-0.14	-62.5	-62.2	C_L	-62.6
1	$\frac{1}{2}$	$-1\Leftrightarrow0$	$+45.59$	-6.39	-0.39	$+38.8$	$+39.0$	B_R	$+39.0$
1	$-\frac{1}{2}$	$0\Leftrightarrow1$	-86.39	-10.89	$+0.40$	-96.9	-98.7	E_L	-96.3
1	$-\frac{1}{2}$	$-1\Leftrightarrow0$	$+18.31$	$+3.38$	$+0.30$	$+22.0$	$+23.2$	A_R	$+22.8$
0	$\frac{1}{2}$	$0\Leftrightarrow1$	$+77.42$	$+0.1$	-0.33	$+77.2$	75.9	D_R	$+78.0$
0	$\frac{1}{2}$	$-1\Leftrightarrow0$	-131.98	-13.55	-0.22	-145.8	-145.9	F_L	145.4
0	$-\frac{1}{2}$	$0\Leftrightarrow1$	$+131.98$	-12.62	$+0.22$	$+119.6$	$+118.8$	F_R	119.3
0	$-\frac{1}{2}$	$-1\Leftrightarrow0$	-77.42	$+0.1$	$+0.33$	-77.0	-77.7	D_L	-77.8
-1	$\frac{1}{2}$	$0\Leftrightarrow1$	-18.31	$+3.41$	-0.30	-15.2	-15.0	A_L	-16.0
-1	$\frac{1}{2}$	$-1\Leftrightarrow0$	$+86.39$	-10.40	-0.40	$+75.6$	$+75.9$	E_R	$+75.1$
-1	$-\frac{1}{2}$	$0\Leftrightarrow1$	-45.59	-6.55	$+0.39$	-51.8	-51.5	B_L	-51.9
-1	$-\frac{1}{2}$	$-1\Leftrightarrow0$	$+59.11$	-3.15	$+0.14$	$+56.1$	$+55.8$	C_R	$+56.2$

action constant $\mu_D E = e^2qQ/4$. These energy levels are given in Table VII which is complete up through the third order of the perturbation theory expanded about the strong field levels. Algebraic expressions for the second- and third-order terms are not given in the tables as the expressions are too clumsy to print. Since these expressions involve the constants H'_D, H'_P, S, and E, the numerical values given in the table were calculated after the constants were known. For our purposes they are most conveniently given in the peculiar energy units gauss-nuclear-magnetons. They can be converted to ergs simply by multiplying by 5.04×10^{-24} erg/gauss/n. m. Just as in D_2, these terms vanish in very high field when the Paschen-Back effect is complete. However, for HD this field must be unusually large to make the magnetic energy of the rotational moment different from that of the deuteron moment by an amount large compared with the other interactions. This is true because the rotational moment (0.660 n. m.) is so nearly equal to the deuteron moment (0.855 n. m.)

Table VIII gives expressions for the positions of the lines accompanying changes of m_D by ±1. This table is derived from Table VII just as was done for the corresponding table (Table III) for D_2.

The simplest procedure to follow in the analysis of this spectrum is to estimate the values of the constants in the theory from the experimental values of the constants obtained with H_2 and D_2 and then to use these constants to predict the positions of the spectral lines. If this procedure proves successful in predicting the observed lines we will automatically have an identification of the lines with the quantum numbers of the transitions between energy levels. Once such an identification has been made we can reverse the process and calculate the values of the constants from the experimentally determined line positions. This direct intercomparison of the constants for the three different molecules is possible because the internuclear distances are almost identical. In fact, the values of $\langle r^{-3}\rangle_{\mathrm{Av}}$ for H_2 and HD differ by only 1 part in 400. This enables us to make an excellent estimate of $S' = \langle 2\mu_P/5r^3\rangle_{\mathrm{Av}} = 13.64$ gauss. Since the electron densities of these molecules depend primarily on the nuclear charge and the internuclear distance, the gradients of the electric field with which the quadrupole moment of the deuteron interacts will be equal in D_2 and HD. The interaction constant E can be taken over directly from H''' of D_2. Similar considerations for the constants H'_D and H'_P are not as certain for two reasons. First, there is no complete quantitative theory for the corresponding constants in H_2 and D_2 which could be modified for HD. And second a naïve theory suffers because of the asymmetry of the HD molecule. For instance, it is not immediately evident that H'_D should equal H'_P and this question does not arise for H_2 or D_2. However, we know that the rotational magnetic moments of H_2, HD, and D_2 are 0.88, 0.66 and 0.44 nuclear magneton, respectively[11] and these quantities are in inverse ratio to the reduced masses of these molecules. We also know that $(H')_{H_2}$ is 27.2 gauss and $(H')_{D_2}$ is 14.0 gauss again in inverse ratio to the reduced masses. We therefore assume that $H'_D = H'_P = 20.4$ gauss.

The values indicated above have been substituted into the formulas for the first-, second-, and third-order perturbations for the D nuclear transitions of HD. The results of these calculations are shown in Table IX. The column marked "Total" is simply the sum of the entries in the three columns to the left of it. The experimental values and their designations are placed so that they correspond most nearly to the calculated values. The agreement in all but two cases is good. The two experimental values which do not agree with the calculated perturbations are necessarily poor because they are merely the center of gravity of a pair of unresolved lines. No further argument, then, is necessary in justification of the assignment of the quantum numbers of the transitions to the experimental lines.

Evaluation of the constants H'_P, S' and E from the experimental data given in Table IX was made in the following way. The second- and third-order perturbations were evaluated using the preliminary constants from H_2 and D_2. These appear in Table IX. The algebraic expressions for the first-order terms were equated to the experimentally evaluated perturbations diminished by the calculated second- and third-order perturbations. The lines A_R and A_L were omitted from the group for reasons that are immediately

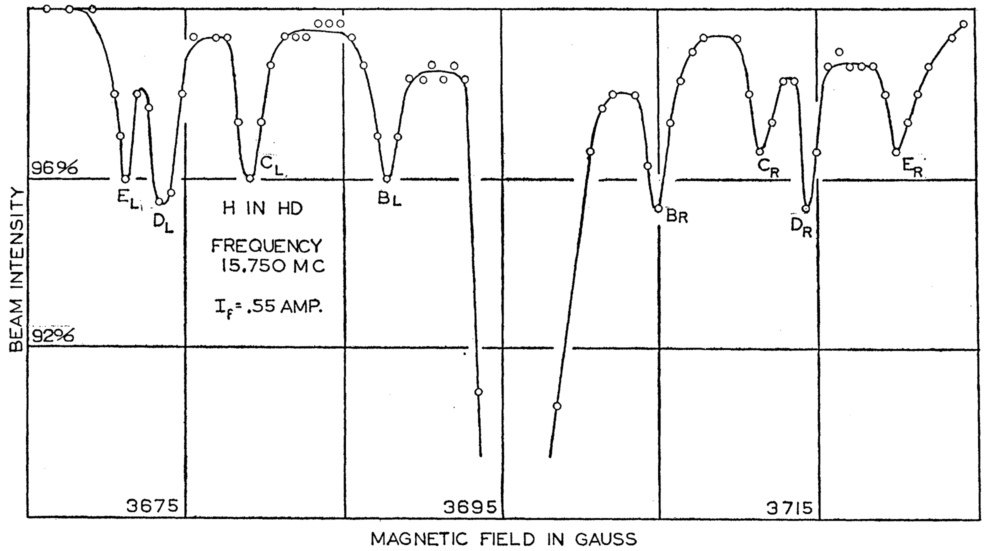

FIG. 4. Radiofrequency spectrum of HD at 80°K for $\Delta m_P = \pm 1$ with m_D and m_J unchanged.

evident in Fig. 3. The experimental lines E_R and D_R were taken together by averaging the theoretical first-order formulas and equating the resulting expression to the displacement of the one unresolved minimum which represents them both. Using this latter equation twice we get ten simultaneous equations which were solved by the method of least squares for the three constants, and we obtain:

$$H'_D = 20.07 \text{ gauss}; \quad S' = 13.348 \text{ gauss}; \quad E = 17.495 \text{ gauss}.$$

The perturbations calculated with these constants are given in Table IX. Agreement with the experimental values is naturally better than with the preliminary values. In fact, except for those minima (A_R, A_L, D_R, E_R) which have already been discussed, the experiment can be regarded as internally consistent to better than 0.5 gauss.

H IN HD

Figure 4 shows the group of minima for changes of m_P of ± 1 at a frequency of 15.750 MC. For these data particular attention has to be paid to the constancy of the homogeneous magnetic fields, while the intensity measurements are made. This is difficult because the intervals between the minima are a very small fraction of the total field. In fact, for the data to be of real quantitative value comparable with the other results of this set of experiments it was necessary to hold the field constant to 0.2 gauss in 3700 gauss. This implies that the field excitation current had to be adjusted and read to 0.01 amp. in 200 amp. Further the slight hysteresis in the electromagnet makes it necessary to vary the current in only one direction during a set of measurements. Because of the slowness of the action of the Pirani gauge detector (15 sec. per deflection and nine deflections per point) at least five hours is required to take one experimental curve. These requirements taxed the rheostat control and storage battery bank to their limit. It can be seen in Table X why it was not expedient to take these measurements at much lower field values where these experimental difficulties would be reduced proportionately. Control and measurement of the radiofrequency were not difficult because of the stability of the r.f. oscillator and the ease of using the General Radio No. 620A wave meter.

Reference to Fig. 4 shows that besides the deep central minimum there are eight small minima for $J = 1$, whereas it is stated above that there should be nine. It will be shown presently that the theory predicts that one of the small ones should be in the position occupied by the deep central minimum, and therefore completely hidden.

The procedure followed in the analysis of the

H nuclear spectrum of HD is entirely similar to the procedure previously outlined for the analysis of the spectrum of D in HD. Table X, which is obtained from Table VII and the relationship $hf_0=2\mu_P H_0$, gives the expressions for the positions of the H in HD lines. The constants involved here are H'_P and $S''=\frac{1}{5}\langle\mu_D/r^3\rangle_{\text{Av}}$. A preliminary value of H'_P is found by taking $H'_P=H'_D=20.4$ gauss as in the case of D in HD. The value of $5S''$ may be estimated from $(\mu_D/r^3)=(\mu_D/\mu_P)(H'')_{\text{H}_2}=10.45$ gauss. These constants substituted in the expressions given in Table X yield the predicted perturbations listed in Table XI. It is there evident that the "Total" predicted perturbation is in excellent agreement with the experimental value. The assignment of the quantum numbers to the experimental lines is therefore accomplished.

The line expected at -1.98 gauss is completely hidden by the central minimum. The other eight minima are clearly resolved and can be used to form eight simultaneous equations for evaluating the two constants H'_P and S'' (see Table X). The values obtained by the method of least squares are $H'_P=20.48$ gauss and $S''=2.12$ gauss. Using these values to recalculate the positions of the minima we get the last column of Table XI. The internal consistency of this set of data is well within the limit of 0.2 gauss.

THEORY OF ENERGY LEVELS

$\mathbf{D_2}$

The energy levels of the D_2 molecule in the state $J=1$ and situated in an external magnetic field H, taken in the direction of the z axis, are given by the characteristic values of the operator

$$\begin{aligned}\mathcal{H}=&-\mu_D(\mathbf{i}_1+\mathbf{i}_2)_z H-\mu_R J_z H-\mu_D H'(\mathbf{i}_1+\mathbf{i}_2)\cdot\mathbf{J}\\&+(\mu_D{}^2/r^3)[\mathbf{i}_1\cdot\mathbf{i}_2-3(\mathbf{i}_1\cdot\mathbf{r})(\mathbf{i}_2\cdot\mathbf{r})/r^2]\\&+\frac{e^2qQ}{2J(2J-1)i(2i-1)}\sum[3(\mathbf{i}\cdot\mathbf{J})^2\\&+\tfrac{3}{2}(\mathbf{i}\cdot\mathbf{J})-i(i+1)J(J+1)],\end{aligned}\qquad(2)$$

where $\mathbf{i}_1$ and $\mathbf{i}_2$ are the spin operators for the two deuteron spins, r is the internuclear distance, and the other symbols have their usual meanings.

The first and second terms represent the effect

TABLE X. *Magnetic fields for which resonances will occur for changes of orientation of the proton spin in* HD *molecules in the first rotational state.* $H_0=hf_0/2\mu_P$. $S''=\langle\mu_D/5r^3\rangle_{\text{Av}}$.

			Magnetic fields for which resonances occur			
m_J	m_P	m_D		First order	Second order	Third order
1	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	1	H_0	$-H'_P\ +2S''$	$-109/H$	
1	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	0	H_0	$-H'_P$	$-4270/H$	$+1.15\times10^6/H^2$
1	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	-1	H_0	$-H'_P\ -2S''$	$+1250/H$	$+2.57\times10^6/H^2$
0	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	1	H_0	$-4S''$	$+3460/H$	$-1.15\times10^6/H^2$
0	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	0	H_0		$-3880/H$	
0	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	-1	H_0	$+4S''$	$+3460/H$	$+1.15\times10^6/H^2$
-1	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	1	H_0	$+H'_P\ +2S''$	$+1250/H$	$-2.57\times10^6/H^2$
-1	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	0	H_0	$+H'_P$	$-4270/H$	$-1.15\times10^6/H^2$
-1	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	-1	H_0	$+H'_P\ -2S''$	$-109/H$	

TABLE XI. *Collected data on H in* HD. *Frequency 15.750 MC.*

			Perturbations						
			Predicted from H_2 and D_2 constants						
m_J	m_P	m_D	First order	Second order	Third order	Total	Experimental value	Line designation	Perturbations from HD constants
1	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	1	-16.22	-0.03	0.00	-16.25	-16.09	C_L	-16.27
1	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	0	-20.40	-1.15	0.08	-21.47	-21.64	D_L	-21.55
1	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	-1	-24.58	0.34	0.18	-24.06	-24.11	E_L	-24.20
0	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	1	-8.36	0.93	-0.08	-7.51	-7.57	B_L	-7.63
0	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	0	0.00	-1.98	0.00	-1.98		A	
0	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	-1	8.36	0.93	0.08	9.37	9.55	B_R	9.49
-1	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	1	24.58	0.34	-0.18	24.74	24.95	E_R	24.88
-1	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	0	20.40	-1.15	-0.08	19.17	19.22	D_R	19.25
-1	$-\frac{1}{2}\leftrightarrow\frac{1}{2}$	-1	16.22	-0.03	0.00	16.19	16.37	C_R	16.21

of the external field on the deuteron and rotational magnetic moments, respectively. The third term is the "spin orbit" interaction of the deuteron magnetic moments with the molecular rotation, and the coupling constant H' has the significance of the magnetic field produced by the rotation at the location of the nuclei. The fourth term is the familiar dipole-dipole interaction between the two nuclear magnets.

The last term represents the effect of the nuclear quadrupole moment and is summed over both nuclei. The quantity q has a meaning similar to that of Eq. (1).

In the appendix it will be shown that for identical nuclei the fourth term may be written as

$$\left\{\frac{I(I+1)+4i_1(i_1+1)}{(2I-1)(2I+3)(2J-1)(2J+3)}\right\} \times\left[3(\mathbf{I}\cdot\mathbf{J})^2+\tfrac{3}{2}(\mathbf{I}\cdot\mathbf{J})-I(I+1)J(J+1)\right]\frac{\mu_D{}^2}{r^3}, \quad (3)$$

where I is the total spin for both deuterons, which is 1 in our case, and i_1, the spin of the individual nucleus, is also 1. The factor in curly brackets is therefore $\frac{2}{5}$. It will also be shown that for the case of total spin $I=1$, the summation in Eq. (2) is equal to the negative of the operator in square brackets in formula 3. *Thus the total quadrupole moment effect is as if we had one nucleus with a nuclear spin of 1 and a quadrupole moment of sign opposite to that of the quadrupole moment of the actual particles.*[12a]

Putting in the values of I and J we may therefore write Eq. (2) as

$$\mathcal{H}=-\mu_D m_I H-\mu_R m_J H-\mu_D H'\mathbf{I}\cdot\mathbf{J} +\left\{\frac{2\mu_D{}^2}{5r^3}-\frac{e^2qQ}{2}\right\}\left[3(\mathbf{I}\cdot\mathbf{J})^2+\tfrac{3}{2}(\mathbf{I}\cdot\mathbf{J}) -I(I+1)J(J+1)\right]. \quad (4)$$

From this form it appears that a quadrupole moment effect cannot be distinguished from dipole-dipole interaction between the two nuclei.

For purposes of convenience we will write $\{2\mu_D{}^2/5r^3-\frac{1}{2}e^2qQ\}$ as $(2\mu_D/5)(H''+H''')$, where $H''=\mu_D/r^3$, and $H'''=-5e^2qQ/4\mu_D$. H'' and H''' may be expressed in gauss and are a measure of the magniture of their respective interactions.

In an infinitely strong field (complete Paschen-Back) the diagonal elements of $\mathcal{H}$ give the value of the energy levels of the molecule. These diagonal elements are given by the formula (see appendix)

$$\mathcal{H}(m_I m_J)=-\mu_D m_I H-\mu_R m_J H-\mu_D H' m_I m_J +\frac{\mu_D}{5}(H''+H''')\left[3m_I{}^2-I(I+1)\right] \times\left[3m_J{}^2-J(J+1)\right]. \quad (5)$$

when we set $I=1$ and $J=1$.

If H is not infinitely great these formulae hold only approximately and must be corrected for the effect of the off-diagonal matrix elements. The energy levels including their perturbations are listed in Table I. The necessary calculations are indicated in the appendix.

HD

For the HD molecule the calculation is somewhat lengthier. The energy expression is

$$\mathcal{H}=-2\mu_P m_P H-\mu_D m_D H-\mu_R m_J H -2\mu_P H'_P(\mathbf{i}_1\cdot\mathbf{J})-\mu_D H'_D(\mathbf{i}_2\cdot\mathbf{J}) +\frac{2\mu_P\mu_D}{r^3}\left[\mathbf{i}_1\cdot\mathbf{i}_2-\frac{3(\mathbf{i}_1\cdot\mathbf{r})(\mathbf{i}_2\cdot\mathbf{r})}{r^2}\right] +\frac{e^2qQ}{2J(2J-1)i_2(2i_2-1)}\left[3(\mathbf{i}_2\cdot\mathbf{J})^2 +\tfrac{3}{2}(\mathbf{i}_2\cdot\mathbf{J})-i_2(i_2+1)J(J+1)\right], \quad (6)$$

where i_1 and i_2 are the proton and the deuteron spins, respectively, and H'_P and H'_D the spin orbit constants for the proton and deuteron which need not necessarily be the same; m_P, m_D, and m_R are the magnetic quantum numbers of the proton, deuteron, and rotation, respectively.

We may write

$$(2\mu_P\mu_D/r^3)\left[\mathbf{i}_1\cdot\mathbf{i}_2-\frac{3(\mathbf{i}_1\cdot\mathbf{r})(\mathbf{i}_2\cdot\mathbf{r})}{r^2}\right] =\frac{\mu_P\mu_D}{r^3}\frac{2}{(2J+3)(2J-1)}\left[3(\mathbf{i}_1\cdot\mathbf{J})(\mathbf{i}_2\cdot\mathbf{J}) +3(\mathbf{i}_2\cdot\mathbf{J})(\mathbf{i}_1\cdot\mathbf{J})-2\mathbf{i}_1\cdot\mathbf{i}_2 J(J+1)\right]. \quad (7)$$

[12a] We are indebted to Dr. Nordsieck for bringing this to our attention.

TABLE XII. *Summary of results. All quantities in gauss.*

	(μ_P/r^3)	(μ_D/r^3)	SPIN-ORBIT CONSTANT	$(-5e^2qQ/4\mu_D)$
m_I in H_2	34.1		27.2	
m_I in D_2		*10.6*	14.0±0.6	87.5±1
m_D in HD	33.4±1	*10.24*	20.1±1.	87.5±1
m_P in HD	*34.5*	10.60±0.2	20.48±0.2	

The diagonal elements of (6) for infinitely strong fields are therefore

$$\begin{aligned}\mathcal{H}(m_Pm_Dm_J)=&-2\mu_Pm_PH-\mu_Dm_DH-\mu_Rm_JH\\&-2\mu_PH'_Pm_Pm_J-\mu_DH'_Dm_Dm_J\\&+\tfrac{4}{5}\mu_PH''[3m_J^2-J(J+1)]m_Pm_D\\&-\tfrac{1}{5}\mu_DH'''[3m_J^2-J(J+1)][3m_D^2-i_2(i_2+1)].\end{aligned}\quad(8)$$

when we use the same definition of H'' and H''' as in Eq. (5). The values of i_2 and J are each equal to 1.

These elements together with their perturbations are listed in Table VII.

RESULTS

Table XII is a summary of the constants obtained from the experiments on H_2, D_2 and HD in the state $J=1$. The quantities have the dimensions of magnetic field and the results are given in gauss. Each row gives the final results obtained from the spectrum which arises from the indicated transition. The first row gives the results of paper I. The second row gives the results obtained from the 6-line spectrum of D_2, and the third and fourth rows the results of the two spectra in HD. The italicized quantity 10.6 in the second row is the value of μ_D/r^3 from the fourth row. This quantity is subtracted from the sum $[\mu_D/r^3-(5e^2qQ/4\mu_D)]$ which is measured experimentally to obtain the quantity in the fourth column. Similarly the italicized quantities μ_D/r^3 and μ_P/r^3 in the third and fourth rows are obtained by multiplying the directly measured values of μ_P/r^3 and μ_D/r^3 by the accurate ratios μ_D/μ_P and μ_P/μ_D, respectively, as obtained from the previous paper. These are entered in the table for the purpose of comparison.

From the quantities given in the first two columns one may calculate the nuclear magnetic moments in question. The results agree with the previously published[10] values of the proton and deuteron moments as is evident from the small variations of the numbers in the first two columns.

The quadrupole moment of the deuteron is calculated from the results of the fourth column. We precede this calculation with a discussion of the determination of the sign of the moment.

In the detailed discussion of the nuclear spectrum of D_2 the following argument was advanced to lead to a positive value of the sign of H'''. The D_2 spectrum requires that H' and S_D have the same sign, and, since H' has the value predicted from the H_2 spectrum, H' is most likely positive. Therefore S_D and H''' are positive. The only seeming weak point in this argument is the sign of H', but it is almost inconceivable that it be negative.

However, the D nuclear spectrum of HD permits us to be certain even with regard to this point. Let us make the violent assumption that H' for the D_2 molecule is negative. Consequently S_D is also negative. The internal consistency of the D_2 nuclear spectrum is not affected by this assumption. We would therefore have $S_D=-98.10$ gauss, and since H'' is positive and equals 10.5 gauss, the quantity $H'''=-108.6$ gauss. For HD we now have the quantity $6E=6H'''/5=-130.3$ gauss. This value combined with $2S'=+26.7$ gauss gives 157.0 gauss for the first-order term for the line with quantum numbers $(0, -\frac{1}{2}, -1\rightarrow 0)$. The second-order perturbation is positive and the other perturbations are negligible. Therefore a line is predicted *at least* as far from the center as 157 gauss. Experimentally the largest observed positive displacement is 118.8 gauss, and this line, of course, fits with the assumption that H''' is positive. Therefore we conclude that H''' is positive.

The measured value of $(-5e^2qQ/4\mu_D)$ is 87.5 gauss from Table XII. In a forthcoming paper, one of us (N.F.R., Jr.) will present data obtained from the analysis of the spectra of D_2 and HD arising from the transitions $m_J=\pm 1$. If we include these values in the average the quantity becomes 87.2±0.5 gauss.

To calculate Q the value of q must be inserted. Nordsieck[12] has calculated the quantity $q'=1/R^3$

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[12] A. Nordsieck, Phys. Rev. **57**, 556(A) (1940).

$-\int \rho d\tau (3\cos^2\theta - 1)/r^3$ for the deuterium molecule. In this expression R is the internuclear distance and the integral is taken over the electronic wave function of the deuterium molecule; r is the distance of the electron from the nucleus and θ is the angle which r makes with the internuclear axis. Thus q' is $\frac{1}{2}\partial^2 V/\partial z^2$. Since our q is defined with respect to the rotational state of the molecule $m=J=1$, it is related to q' by $q=-2Jq'/(2J+3)=-2q'/5$. Nordsieck's value of q' is 1.193×10^{24} cm^{-3}, i.e., the effect of the positive nuclear charge is greater than the combined effect of the two electrons. Since $H'''=-5e^2qQ/4\mu_D$ has been shown to be positive and since q is negative, Q the nuclear quadrupole moment is positive. Thus

$$Q=\frac{87.2\times0.855\times5.04\times10^{-24}\times2}{4.80^2\times10^{-20}\times1.193\times10^{24}}$$

and therefore $Q=2.73\times10^{-27}$ cm^2.

This value is more precise than the value previously reported[1] because of the refinement of the experiments and the refinement of Nordsieck's calculation of q. The chief source of error is in q.

Discussion

The positive sign of the quadrupole moment of the deuteron shows that the charge distribution is that of a prolate spheroid spinning about its major axis. Most of the other known nuclear quadrupole moments also show this surprising property.

Although the quadrupole moment of the deuteron, 2.73×10^{-27} cm^2, is the smallest value yet reported for any nucleus, it does not mean that the deuteron is exceptional. It must be remembered that the optical methods which have been used to study other nuclei are not sensitive enough to detect quadrupole moments very much smaller than 10^{-25} cm^2. Furthermore, it should be noted from the definition of Q, $eQ=e\int\rho(3z^2-r^2)d\tau$, that for a given asymmetry, i.e., a given value of $3z^2/r^2$, the larger nuclei should have larger quadrupole moments. Moreover, more than one nuclear charge may contribute to the moment. In fact for the heavier nuclei some of the quadrupole moments are so large that this must necessarily be the case. It would perhaps be more revealing to consider Q/Z rather than Q itself for purposes of comparison.

It may be of interest to calculate the quantity $3z^2/r^2$ which is a rough measure of the departure of the deuteron from spherical symmetry. We write $3z^2/r^2=1+Q/r^2$. For r^2 we take the average squared distance of the proton from the centroid of the deuteron. This quantity calculated from the deuteron wave function[13] is 2.38×10^{-26}. The value of $3z^2/r^2$ is therefore 1.115.

It is of importance to consider whether the effect which we ascribe to the presence of a quadrupole moment in the deuteron can be due to some other form of interaction between the deuteron spin and the molecular rotation. The experimental result which is observed is an interaction of the dipole-dipole form. As J. H. Van Vleck has pointed out to us, such effects can arise in the second-order interaction of the nuclear spin with the electrons of the molecule. However, the excellent agreement of the values of the proton moment, as obtained directly, and from the analysis of the H_2 spectrum in which the moment is evaluated from the dipole-dipole interaction, precludes this possibility. This point of view receives further support from the results presented in this paper, which also show that the dipole-dipole interaction in HD is exactly the magnitude to be expected from the known values of the nuclear moments. To this evidence must be added the experimental proof that the electronic wave functions of H_2, D_2, and HD are not greatly changed because of the differences in their moments of inertia, as is shown by the fact that the rotational magnetic moments[11] are closely proportional to the angular velocities of rotation in the state $J=1$. This is likewise true for the spin-orbit coupling which, as has been pointed out, may be considered as the magnetic field produced by the rotation of the molecule at the positions of the nuclei.

As has been suggested by Schwinger,[14] the presence of a quadrupole moment in the deuteron indicates that the ground state of the deuteron is not a $^3S_1$ state but may be a mixture of $^3S_1$

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[13] H. Bethe and R. Bacher, Rev. Mod. Phys. **8**, 112 (1936) (Eqs. (44a) and (44c)).

[14] J. Schwinger, Phys. Rev. **55**, 235 (1939).

and $^3D_1$. On this view the deuteron magnetic moment will be a resultant of the contributions not only of the spin moments of the proton and neutron but also of the orbital moment of the proton. If the moments of the proton and neutron were strictly additive, the effect of the quadrupole moment would result in a seeming departure from this additivity in that the deuteron moment would not be just the sum of the proton and neutron moments.

Fortunately it is possible to make this interesting comparison because of the recent measurement of the neutron moment by Alvarez and Bloch.[15] Within the experimental errors the sum of the moments of the proton and the neutron is equal to that of the deuteron. Whether this apparent additivity conceals a real nonadditivity will not be known until an adequate theory of the deuteron is given which accounts quantitatively for all the known facts including the magnitude of the quadrupole moment.

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Appendix

The magnetic dipole-dipole interaction of Eq. (2) of the text contains the operator $[(\mathbf{i}_1\cdot\mathbf{i}_2)r^2-3(\mathbf{i}_1\cdot\mathbf{r})(\mathbf{i}_2\cdot\mathbf{r})]/r^2$. If we introduce the total nuclear spin $\mathbf{I}=\mathbf{i}_1+\mathbf{i}_2$ this expression can be written as

$$\{\tfrac{1}{2}[\mathbf{I}^2r^2-3(\mathbf{I}\cdot\mathbf{r})^2]-\tfrac{1}{2}[\mathbf{i}_1^2r^2-3(\mathbf{i}_1\cdot\mathbf{r})^2]-\tfrac{1}{2}[\mathbf{i}_2^2r^2-3(\mathbf{i}_2\cdot\mathbf{r})^2]\}/r^2. \tag{9}$$

By a general theorem[16] we can write

$$\begin{aligned}
&\text{(a)} && \frac{(x+iy)^2}{r^2}=-\frac{2}{(2J-1)(2J+3)}(J_x+iJ_y)^2,\\
&\text{(b)} && \frac{z(x+iy)}{r^2}=-\frac{2}{(2J-1)(2J+3)}\tfrac{1}{2}[J_z(J_x+iJ_y)+(J_x+iJ_y)J_z],\\
&\text{(c)} && \frac{3z^2-r^2}{r^2}=-\frac{2}{(2J-1)(2J+3)}(3J_z^2-J_x^2-J_y^2-J_z^2).
\end{aligned} \tag{10}$$

When formula 9 is expanded and Eqs. (10) substituted it becomes

$$-\frac{1}{(2J-1)(2J+3)}\{[\mathbf{I}^2\mathbf{J}^2-\tfrac{3}{2}(\mathbf{I}\cdot\mathbf{J})-3(\mathbf{I}\cdot\mathbf{J})^2]-[\mathbf{i}_1^2\mathbf{J}^2-\tfrac{3}{2}(\mathbf{i}_1\cdot\mathbf{J})-3(\mathbf{i}_1\cdot\mathbf{J})^2]-[\mathbf{i}_2^2\mathbf{J}^2-\tfrac{3}{2}(\mathbf{i}_2\cdot\mathbf{J})-3(\mathbf{i}_2\cdot\mathbf{J})^2]\}. \tag{11}$$

If i_1 and i_2 are equal, then for all matrix elements, m_I, m_J, I, $J\rightarrow m_I'$, m_J', I, J, this operator is equivalent to the operator

$$-\frac{I(I+1)+4i_1(i_1+1)}{(2I-1)(2I+3)(2J-1)(2J+3)}[\mathbf{J}^2\mathbf{I}^2-\tfrac{3}{2}(\mathbf{J}\cdot\mathbf{I})-3(\mathbf{J}\cdot\mathbf{I})^2] \tag{12}$$

for any value of the total spin I. There are matrix elements where $\Delta I=2$ which can be obtained from formula 11 but not from formula (12). For D_2 in the state $I=1$ these additional terms do not exist.

The coefficient multiplying the operator is obtained by using the expressions for the matrix elements of the spins i_1 and i_2 when combined to give a total spin $\mathbf{I}$.[17]

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[15] L. Alvarez and F. Bloch, Phys. Rev. 57, 111 (1940).

[16] H. A. Bethe, *Handbuch der Physik*, Vol. 24, No. 1, Eq. (65.36).

[17] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, 1935), Chapter III.

To show the total effect of the two deuteron quadrupole moments in Eq. (2) of the text we simply add the two operators in the sum. From Eqs. (11) and (12) this operator becomes

$$\left[1-\frac{I(I+1)+4i_1(i_1+1)}{(2I-1)(2I+3)}\right][\mathbf{J}^2\mathbf{I}^2-\tfrac{3}{2}(\mathbf{J}\cdot\mathbf{I})-3(\mathbf{J}\cdot\mathbf{I})^2]. \tag{13}$$

For the special case of D_2, $i_1=i_2=1$, $I=1$, the first parenthesis of 13 is equal to -1. Thus it is seen that the combined effect of the two deuterons is equivalent to that of a single spin of unity with a quadrupole moment of opposite sign.

The matrix elements of

$$F=3(\mathbf{I}\cdot\mathbf{J})^2+\tfrac{3}{2}(\mathbf{I}\cdot\mathbf{J})-I(I+1)J(J+1) \tag{14}$$

are easily written down from the expansion

$$\begin{aligned}F=\tfrac{1}{2}[3J_z^2-J(J+1)][3I_z^2-I(I+1)]+\tfrac{3}{4}[J_z(J_x+iJ_y)+(J_x+iJ_y)J_z][I_z(I_x-iI_y)+(I_x-iI_y)I_z]\\ +\tfrac{3}{4}[J_z(J_x-iJ_y)+(J_x-iJ_y)J_z][I_z(I_x+iI_y)+(I_x+iI_y)I_z]\\ +\tfrac{3}{4}[(I_x+iI_y)^2(J_x-iJ_y)^2+(I_x-iI_y)^2(J_x+iJ_y)^2].\end{aligned} \tag{15}$$

Utilizing the rules of matrix multiplication and the matrix elements of angular momentum,

$$\begin{aligned}(m|L_z|m)&=m,\\ (m|L_x+iL_y|m-1)&=[(L+m)(L-m+1)]^{\frac{1}{2}},\\ (m|L_x-iL_y|m+1)&=[(L-m)(L+m+1)]^{\frac{1}{2}},\end{aligned} \tag{16}$$

we obtain all the matrix elements of F. The first term on the right-hand side of 15 gives all the diagonal elements; the second and third all the elements where $m_J, m_I\rightarrow m_J\pm 1, m_I\mp 1$; and the last two terms the elements $m_J, m_I\rightarrow m_J+2, m_I-2$ and m_J-2, m_I+2, respectively. These elements are

$$\begin{aligned}(m_Jm_I|F|m_Jm_I)&=\tfrac{1}{2}[3m_I^2-I(I+1)][3m_J^2-J(J+1)],\\ (m_Jm_I|F|m_J-1m_I+1)&=\tfrac{3}{4}(2m_J-1)(2m_I+1)[(J+m_J)(J-m_J+1)(I-m_I)(I+m_I+1)]^{\frac{1}{2}},\\ (m_Jm_I|F|m_J+1m_I-1)&=\tfrac{3}{4}(2m_J+1)(2m_I-1)[(J-m_J)(J+m_J+1)(I+m_I)(I-m_I+1)]^{\frac{1}{2}},\\ (m_Jm_I|F|m_J-2m_I+2)&=\tfrac{3}{4}[(J+m_J)(J+m_J-1)(J-m_J+1)(J-m_J+2)(I-m_I)\\ &\qquad\times(I-m_I-1)(I+m_I+1)(I+m_I+2)]^{\frac{1}{2}},\\ (m_Jm_I|F|m_J+2m_I-2)&=\tfrac{3}{4}[(J-m_J)(J-m_J-1)(J+m_J+1)(J+m_J+2)\\ &\qquad\times(I+m_I)(I+m_I-1)(I-m_I+1)(I-m_I+2)]^{\frac{1}{2}},\end{aligned} \tag{17}$$

These elements are evaluated for D_2 by setting $I=J=1$.

In the case of HD there is no total spin angular momentum. We multiply up the expression in the bracket of the right-hand side of Eq. (7) and write

$$\begin{aligned}G&=3(\mathbf{i}_1\cdot\mathbf{J})(\mathbf{i}_2\cdot\mathbf{J})+3(\mathbf{i}_2\cdot\mathbf{J})(\mathbf{i}_1\cdot\mathbf{J})-2\mathbf{i}_1\cdot\mathbf{i}_2J(J+1)\\ &=2i_z^1i_z^2[3J_z^2-J(J+1)]-\tfrac{1}{2}[(i_x^1+ii_y^1)(i_x^2-ii_y^2)+(i_x^1-ii_y^1)(i_x^2+ii_y^2)][3J_z^2-J(J+1)]\\ &\quad+\tfrac{3}{2}[i_z^1(i_x^2-ii_y^2)+i_z^2(i_x^1-ii_y^1)][J_z(J_x+iJ_y)+(J_x+iJ_y)J_z]\\ &\quad+\tfrac{3}{2}[i_z^1(i_x^2+ii_y^2)+i_z^2(i_x^1+ii_y^1)][J_z(J_x-iJ_y)+(J_x-iJ_y)J_z]\\ &\quad+\tfrac{3}{2}(i_x^1+ii_y^1)(i_x^2+ii_y^2)(J_x-iJ_y)^2+\tfrac{3}{2}(i_x^1-ii_y^1)(i_x^2-ii_y^2)(J_x+iJ_y)^2.\end{aligned} \tag{18}$$

The matrix elements are obtained with the use of the relations of Eqs. (16). The letter i without subscripts is $\sqrt{-1}$. For the particular case of HD we set $i_1=\frac{1}{2}$, $i_2=1$, and $J=1$. The spin orbit interactions of the form $I\cdot J$ are obtained in the usual manner by setting

$$I\cdot J=I_zJ_z+\tfrac{1}{2}(I_x+iI_y)(J_x+iJ_y)+\tfrac{1}{2}(I_x-iI_y)(J_x+iJ_y)$$

together with Eqs. (16).

The perturbations of the energy levels of Eqs. (5) and (8) are obtained from the matrix elements by the usual second-order perturbation theory.

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Secondary Emission from Films of Silver on Platinum*

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Total secondary emission and energy distribution of secondary electrons have been measured for films of known thickness of silver on platinum. The depth of origin of the total secondary emission in silver as a function of primary energy, and the depth of origin of secondaries having a given energy were determined. Practically all the secondaries from primaries of 20 ev energy originate at a depth of less than 15 atomic layers, and those from primaries of 50 ev energy originate at a depth of less than 30 atomic layers. For higher primary energies, it was found that an appreciable amount of emission comes from a depth greater than 150 atomic layers. Secondaries with energies close to that of the primaries originate at a depth small compared to that of the low energy secondaries.

Introduction

While the general characteristics of secondary emission from pure metals have been well established, there is lack of agreement among investigations as to the depth at which the secondary electrons originate and as to the relative effects of the work function and the characteristic production of secondaries within the metal. Secondary emission is generally assumed to be dependent on the surface work function through which the electrons must escape and on the production and absorption of electrons within the metal, these two effects being independent and characteristic of the particular metal.

Treloar[1] concludes that a sufficiently thin film of a foreign material on a metal acts chiefly to alter the work function, the emission from the film itself being important only at greater film thickness. Plotting secondary emission against thickness of barium deposited on tungsten, he found an increase in the secondary emission as the work function was lowered to that of barium, the production of secondaries still occurring mostly in the tungsten. At greater thickness of barium film more of the secondaries originated in the film, which has a smaller production than that of tungsten, and the emission decreased, resulting in a maximum in the curve. The thickness at which half the emission came from the film and half from the base metal he estimated as 1.4 atomic layers, the mean depth of origin of secondaries from 300-volt primaries.

Coomes[2] has not observed this maximum for thorium on tungsten, but Bruining[3] has observed it for barium on molybdenum. He found that the photoelectric emission also reached a maximum for the same thickness of barium, indicating that these changes were due in part to the decreasing work function. From experimental work with rough surfaces and from an experimental value of the absorption coefficient,

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